

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Japanese Application of

Osamu YOSHITAKE et al.

Japanese Application No. : 2003-338081

Filing date : September 29, 2003

For :

Organic Electroluminescent Element

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

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- (1) that I know well both the Japanese and English languages;
- (2) that I translated the above-identified Japanese Application from Japanese to English;
- (3) that the attached English translation is a true and correct translation of the above-identified Japanese Application to the best of my knowledge and belief; and
- (4) that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 USC 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereon.

Date : January 9, 2009

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Signature: Nobuyoshi TAKAHASHI

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[Name of Material] Specification 1

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[Name of Material]                      Abstract 1

[General Power of Attorney No.] 9720598

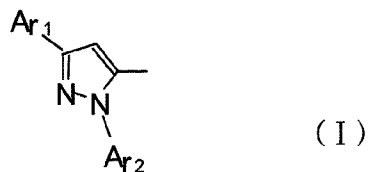
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## [Name of Document] Claims

## [Claim 1]

An organic electroluminescent element comprising an anode, organic layers and a cathode piled one upon another on a substrate wherein at least one of the organic layers is a light-emitting layer containing a host material and a dopant material and a pyrazole-derived compound having 2-4 pyrazole structures represented by the following formula I in the same molecule is used as said host material:

(Chem 1)

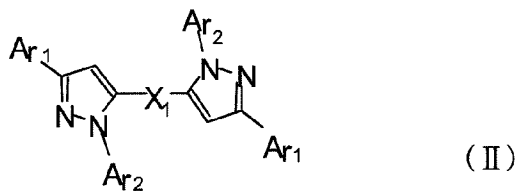


wherein, Ar<sub>1</sub>-Ar<sub>2</sub> are independently hydrogen or substituted or unsubstituted aromatic hydrocarbon groups and at least one of Ar<sub>1</sub>-Ar<sub>3</sub> is a group other than hydrogen.

## [Claim 2]

An organic electroluminescent element as described in claim 1 wherein the pyrazole-derived compound is represented by the following formula II:

(Chem 2)



wherein, Ar<sub>1</sub>-Ar<sub>2</sub> are independently hydrogen or substituted or unsubstituted aromatic hydrocarbon groups, at least one of Ar<sub>1</sub>-Ar<sub>2</sub> is a group other than hydrogen and X<sub>1</sub> is a direct bond or a substituted or unsubstituted divalent aromatic hydrocarbon group.

[Claim 3]

An organic electroluminescent element as described in claim 2 wherein Ar<sub>1</sub> and Ar<sub>2</sub> are phenyl groups and X<sub>1</sub> is phenylene group in the compound represented by formula II.

[Claim 4]

An organic electroluminescent element as described in any one of claims 1 to 3 wherein the dopant material comprises at least one metal complex selected from phosphorescent ortho-metalated metal complexes and porphyrin metal complexes.

[Claim 5]

An organic electroluminescent element as described in claim 4 wherein the metal complex comprises at least one metal selected from ruthenium, rhodium, palladium, silver, rhenium, osmium, iridium, platinum and gold at its center.

[Claim 6]

An organic electroluminescent element as described in any one of claims 1 to 5 wherein a hole-blocking layer or an electron-transporting layer or both are disposed between the light-emitting layer and the cathode.

[Name of Document] Specification

[Title of the Invention] Organic Electroluminescent Element

[Field of Technology]

[0001]

This invention relates to an organic electroluminescent element and, more particularly, to a thin-film device which emits light when an electrical field is applied to its organic light-emitting layer.

[Background Technology]

[0002]

In the development of electroluminescent elements utilizing organic materials (hereinafter referred to as organic EL element), the kind of electrodes was optimized for the purpose of improving the electron-injecting efficiency from the electrode and an element in which a hole-transporting layer of an aromatic diamine and a light-emitting layer of 8-hydroxyquinoline aluminum complex are disposed as thin films between the electrodes has been developed (Appl. Phys. Lett., Vol. 51, p. 913, 1987) to bring about a noticeable improvement in luminous efficiency over the conventional elements utilizing single crystals of anthracene and the like. Following this, the developmental works of organic EL elements have been focused on their commercial applications to high-performance flat panels characterized by self luminescence and high-speed response.

[0003]

In order to improve the efficiency of such organic EL elements still further, various modifications of the aforementioned basic structure of anode/hole-transporting layer/light-emitting layer/cathode have been tried by suitably adding a hole-injecting layer, an electron-injecting layer and an electron-transporting layer. For example, the following structures are known: anode/hole-injecting layer/hole-transporting layer/light-emitting layer/cathode; anode/hole-injecting layer/light-emitting layer/electron-transporting layer/cathode; and anode/hole-injecting layer/light-emitting

layer/electron-transporting layer/electron-injecting layer/cathode. The hole-transporting layer has a function of transporting the holes injected from the hole-injecting layer to the light-emitting layer while the electron-transporting layer has a function of transporting the electrons injected from the cathode to the light-emitting layer.

[0004]

The interposition of this hole-transporting layer between the light-emitting layer and the hole-injecting layer enables injection of more holes into the light-emitting layer by application of lower electrical field. Furthermore, the electrons injected into the light-emitting layer from the cathode or electron-transporting layer accumulate in the interface between the hole-transporting layer and the light-emitting layer as the hole-transporting layer obstructs transport of electrons and, as a result, the luminous efficiency increases.

Likewise, the interposition of the electron-transporting layer between the light-emitting layer and the electron-injecting layer enables injection of more electrons into the light-emitting layer by application of lower electrical field. Furthermore, the holes injected into the light-emitting layer from the anode or hole-transporting layer accumulate in the interface between the electron-transporting layer and the light-emitting layer as the electron-transporting layer obstructs transport of holes and, as a result, the luminous efficiency increases.

A large number of organic materials conforming to the function of these layered structures have been developed.

[0005]

The aforementioned element comprising the hole-transporting layer of an aromatic diamine and the light-emitting layer of 8-hydroxyquinoline aluminum complex and many other elements utilize fluorescence. Now, the utilization of phosphorescence, that is, emission of light from the triplet excited state, is expected to enhance the luminous efficiency approximately three times that of the conventional elements



utilizing fluorescence (singlet). To achieve this object, studies have been conducted on the use of coumarin derivatives and benzophenone derivatives in the light-emitting layer, but the result was nothing but extremely low luminance. Thereafter, the use of europium complexes was attempted, but it was unable to obtain high luminous efficiency.

[0006]

The possibility of emitting red light at high efficiency by the use of a platinum complex (T-1, PtOEP) is reported in the recent non-patent document 1. Thereafter, it is reported in the non-patent document 2 that the efficiency of emitting green light has been improved markedly by doping the light-emitting layer with an iridium complex (T-2, Ir(Ppy)<sub>3</sub>). It is reported further that optimization of the light-emitting layer enables this and other iridium complexes to show extremely high luminous efficiency even when the structure of a device is simplified.

[0007]

In application of organic EL devices to display devices such as flat panel displays, it is necessary to improve the luminous efficiency and, at the same time, to fully secure the stability during driving. However, the organic electroluminescent devices utilizing the phosphorescent molecule (T-2) described in the non-patent document 2, although highly efficient, do not have sufficient driving stability for practical use at the present time (Jpn. J. Appl. Phys., Vol. 38, p. L1502, 1999).

[0008]

The main cause of the deterioration of the aforementioned driving stability is presumed to be the deterioration of the shape of thin film of the light-emitting layer in the structure of an element such as substrate/anode/hole-transporting layer/light-emitting layer/hole-blocking layer/electron-transporting layer/cathode or substrate/anode/hole-transporting layer/light-emitting layer/electron-transporting layer/anode. It is likely that the deterioration of the shape of thin film is attributable to crystallization (or cohesion) of thin organic amorphous films caused by generation of

heat during driving of the element and poor heat resistance is due to low glass transition temperature ( $T_g$ ) of the material in use.

[0009]

It is described in the non-patent document 2 that a carbazole compound (H-1, CBP) or a triazole compound (H-2, TAZ) is used in the light-emitting layer and a phenanthroline derivative (HB-1) is used in the hole-blocking layer. Because of their high symmetry and low molecular weight, these compounds readily undergo crystallization or cohesion and suffer deterioration of the shape of thin film. Besides, their crystallinity is too high to allow observation of their  $T_g$ . Such instability of the shape of thin film of the light-emitting layer adversely affects the performance of a device, for example, by shortening the driving life and lowering the heat resistance. For the reasons described above, a difficult problem facing phosphorescent organic electroluminescent devices at the present time is their driving stability.

[0010]

It is disclosed in the aforementioned patent literature 1 that a compound containing an oxadiazolyl group is used as a host material in an organic EL element comprising a host material and a phosphorescent dopant material in its light-emitting layer. An organic EL element comprising a thiazole or pyrazole structure in its organic layers is disclosed in patent literature 2. An organic EL element comprising a phosphorescent iridium complex and a carbazole compound in its light-emitting layer is disclosed in patent literature 3. An organic EL element comprising a carbazole compound (PVK), a compound containing an oxadiazolyl group (PBD) and an iridium complex ( $\text{Ir(ppy)}_3$ ) in its light-emitting layer is disclosed in patent literature 4. Ortho-metalated metal complexes and porphyrin metal complexes are proposed as phosphorescent compounds in patent literature 5. However, they face the aforementioned problem. It is to be noted that patent literature 2 discloses no organic EL elements utilizing phosphorescence.

[0011]

[Patent literature 1] JP2002-352957 A

[Patent literature 2] JP2001-230079 A

[Patent literature 3] JP2001-313178 A

[Patent literature 4] JP2003-45611 A

[Patent literature 5] JP2002-158091 A

[Non-patent literature 1] Nature, Vol. 395, p. 151, 1998

[Non-patent literature 2] Appl. Phys. Lett., Vol. 75, p. 4, 1999

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0012]

Enhancement of the luminous efficiency and improvement of the driving stability and heat resistance are essential requirements when applications of phosphorescent organic electroluminescent devices to display devices such as flat panel displays and illuminating devices are considered. An object of this invention is to provide an organic electroluminescent device that shows excellent luminous efficiency by producing higher luminance at lower current density and good driving stability.

[Means to Solve the Problems]

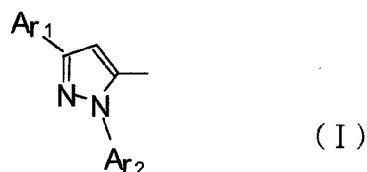
[0013]

The inventors of this invention have conducted intensive studies, found that the use of a specified compound in the light-emitting layer has solved the aforementioned problems, and completed this invention.

[0014]

Accordingly, this invention relates to an organic electroluminescent device comprising an anode, organic layers, and a cathode piled one upon another on a substrate wherein at least one of the organic layers is a light-emitting layer containing a host material and a dopant material and a pyrazole-derived compound having 2 to 4 pyrazole structures represented by the following formula I in the same molecule is used as said host material.

[Chem 1]

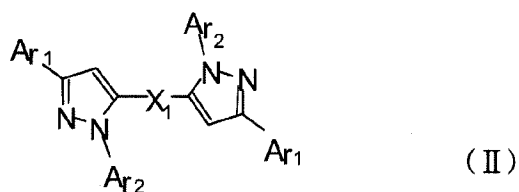


In formula I, Ar<sub>1</sub> and Ar<sub>2</sub> are independently hydrogen or substituted or unsubstituted aromatic hydrocarbon groups.

[0015]

A compound represented by the following formula II is preferable as a pyrazole-derived compound.

[Chem 2]



In formula II, Ar<sub>1</sub> and Ar<sub>2</sub> are independently hydrogen or substituted or unsubstituted aromatic hydrocarbon groups and X<sub>1</sub> is a direct bond or a substituted or unsubstituted divalent aromatic hydrocarbon group.

A compound represented by formula II wherein Ar<sub>1</sub> and Ar<sub>2</sub> are phenyl groups and X<sub>1</sub> is a phenylene group is preferred as a pyrazole-derived compound.

[0016]

A dopant material preferably contains at least one metal complex selected from phosphorescent ortho-metalated metal complexes and porphyrin metal complexes. Preferable organic metal complexes are those containing at least one metal selected from ruthenium, rhodium, palladium, silver, rhenium, osmium, iridium, platinum, and

gold at the center.

[0017]

An organic electroluminescent element of this invention advantageously comprises a hole-blocking layer between a light-emitting layer and a cathod or an electron-transporting layer between a light-emitting layer and a cathode.

[0018]

This invention will be described in detail below.

An organic electroluminescent device (organic EL device) according to this invention comprises organic layers between an anode and a cathode provided on a substrate and at least one of the organic layers is a light-emitting layer containing a specified host material as a primary component and a phosphorescent dopant material as a secondary component.

[0019]

The primary component here means the component which accounts for 50 wt% or more of the materials constituting the layer in question while the secondary component means the rest of the materials. A host material has an excited triplet level higher in energy than that of a dopant material.

[0020]

According to this invention, a compound to be incorporated in the light-emitting layer as a host material is required to form a thin film of stable shape, have a high glass transition temperature ( $T_g$ ) and transport holes and/or electrons efficiently. Further, the compound is required to be electrochemically and chemically stable and rarely generate impurities during manufacture or use which become traps or quench emitted light. As a compound satisfying these requirements, a pyrazole-derived compound having a pyrazole structure represented by the aforementioned formula I is used.

[0021]

In formula I,  $Ar_1$  and  $Ar_2$  are independently hydrogen or substituted or unsubstituted

aromatic hydrocarbon groups and preferably at least one of Ar<sub>1</sub> and Ar<sub>2</sub> is an aromatic hydrocarbon group. Preferable examples of such aromatic hydrocarbon groups are aryl groups having 1 to 3 rings such as phenyl, naphthyl, and anthracenyl groups. These groups may have substituent groups and preferable substituent groups are lower alkyl groups of 1 to 6 carbon atoms such as methyl and ethyl groups and aryl groups of 6 to 12 carbon atoms such as phenyl and methylphenyl groups.

[0022]

As described above, one of the requirements a host material must satisfy is a suitable molecular weight to form a thin film of stable shape and the presence of 2 or more pyrazole structures is desirable. A host material for an organic EI device is generally made into film by vacuum deposition and, in this case, an organic compound having a molecular weight larger than is necessary requires excessive energy in vacuum deposition and decomposition occurs in preference to evaporation. For this reason, the number of pyrazole structures is preferably 4 at most.

[0023]

Preferable pyrazole-derived compounds are those represented by the aforementioned general formula II. In general formula II, Ar<sub>1</sub> and Ar<sub>2</sub> are as defined above and they may change independently.

Furthermore, X1 is a direct bond or a substituted or unsubstituted divalent aromatic hydrocarbon group, preferably a divalent aromatic hydrocarbon group of 1 to 3 rings; concrete examples are groups such as 1,4-phenylene, 1,3-phenylene, 1,4-naphthylene, 1,5-naphthylene, 2,6-naphthylene, 3,3'-biphenylene, 4,4'-biphenylene, and 9,10-anthracenylene. An example of the substituent group is an alkyl group of 1 to 6 carbon atoms.

[0024]

As describe above, a host material is required to have a suitable molecular weight to form a thin film of stable shape and a pyrazole-derived compound selected as a host material is preferably represented by formula II wherein both Ar<sub>1</sub> and Ar<sub>2</sub> are

aromatic hydrocarbon groups. Furthermore, this material is used for fabrication of an organic EL device generally by forming it into film by vacuum deposition and, in this case, an organic compound having a molecular weight larger than is necessary requires excessive energy in vacuum deposition and decomposition occurs in preference to evaporation. For this reason, the aromatic groups  $Ar_1$  and  $Ar_2$  and the aromatic group  $X_1$  are preferably constituted of 1 to 3 rings.

[0025]

On the other hand, suppression of crystallinity is also an important requirement for forming a thin film of stable shape and the crystallinity of organic compounds is considered to be governed by symmetry of the molecular structure (planarity), intermolecular interaction of polar groups, and the like. Introducing aromatic groups to positions 1 and 3 of the pyrazole ring prevents the pyrazole-derived compounds to be used in this invention from assuming a planar molecular structure and suppresses their crystallinity. Furthermore, arranging bulky hydrocarbon groups around strongly polar nitrogen atoms produces an effect of suppressing also the intramolecular interaction.

[0026]

The groups  $Ar_1$  and  $Ar_2$  are preferably hydrogen or substituted or unsubstituted aromatic hydrocarbon groups of 1 to 3 rings; the substituent groups are preferably lower alkyl groups of 1 to 5 carbon atoms and their number is preferably in the range of 0 to 3. Concretely, the following aromatic hydrocarbon groups are preferable; phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,4-dimethylphenyl, 3,4-dimethylphenyl, 2,4,5-trimethylphenyl, 4-ethylphenyl, 4-tert-butylphenyl, 1-naphthyl, 2-naphthyl, 1-anthracenyl, 2-anthracenyl, 9-anthracenyl, and 9-phenanthrenyl. Furthermore,  $Ar_1$  and  $Ar_2$  may be identical with or different from each other.

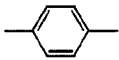


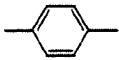

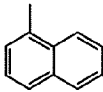


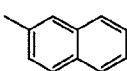
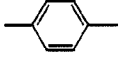
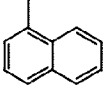

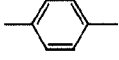
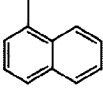
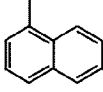
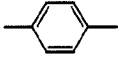
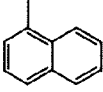
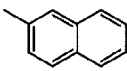
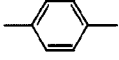
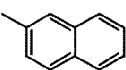

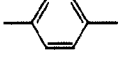
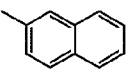
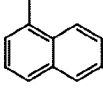
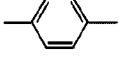
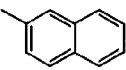
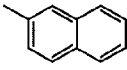
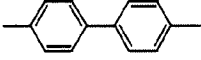


[0027]

Some of the compounds represented by formula II are shown as concrete examples in Tables 1 to 6, but the compounds represented by formula II are not

limited to these examples. The groups  $X_1$ ,  $Ar_1$ , and  $Ar_2$  in the tables correspond to  $X_1$ ,  $Ar_1$ , and  $Ar_2$  in formula II.

[0028]

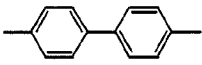

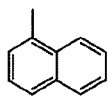
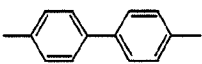

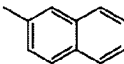
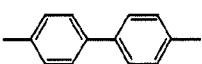
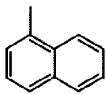

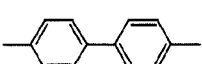
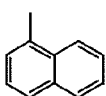
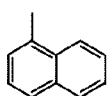
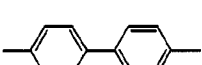
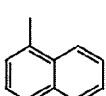
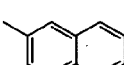
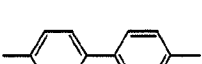
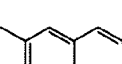

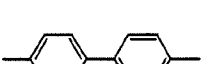
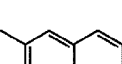
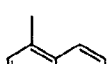
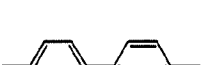
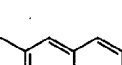
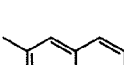
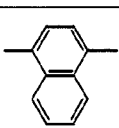


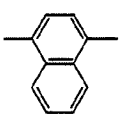

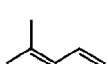
(Table 1)

	$X_1$	$Ar_1$	$Ar_2$
101			
102			
103			
104			
105			
106			
107			
108			
109			
110			



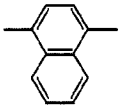

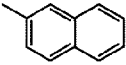
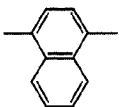
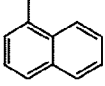

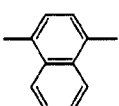
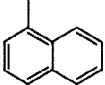
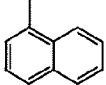
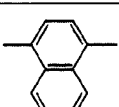
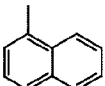
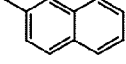
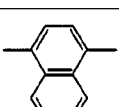
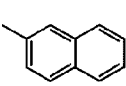

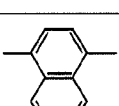
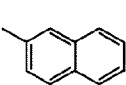
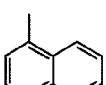
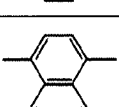
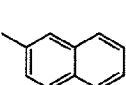
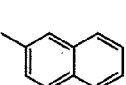
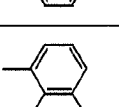


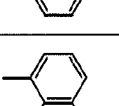

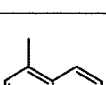
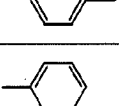

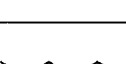
[0029]

(Table 2)

	X1	Ar1	Ar2
111			
112			
113			
114			
115			
116			
117			
118			
119			
120			

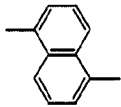
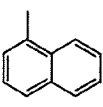

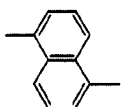
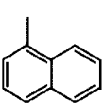
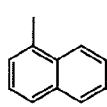
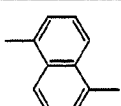
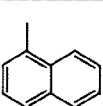
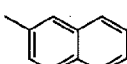
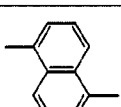
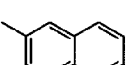

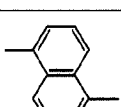
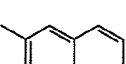
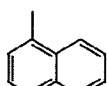
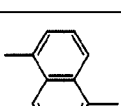
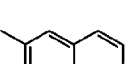
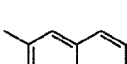
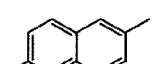


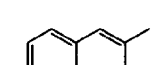

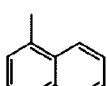
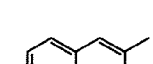

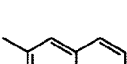
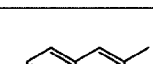
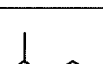

[0030]

(Table 3)

	X1	Ar1	Ar2
121			
122			
123			
124			
125			
126			
127			
128			
129			
130			

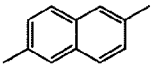
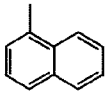
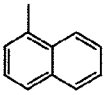
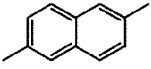
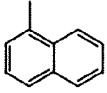
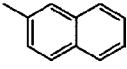
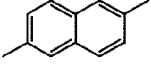
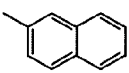

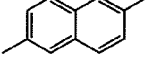
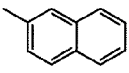
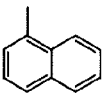
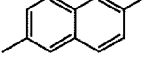
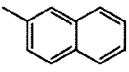
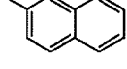
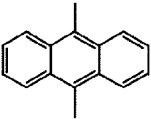


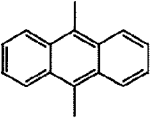

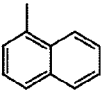
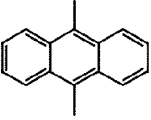

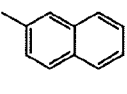
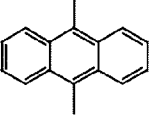
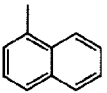

[0031]

(Table 4)

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132			
133			
134			
135			
136			
137			
138			
139			
140			

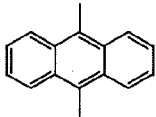
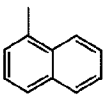
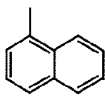
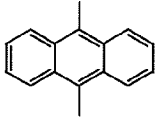
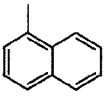
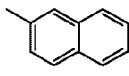
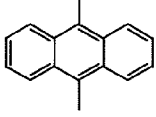
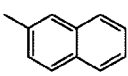

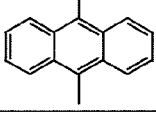
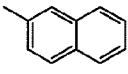
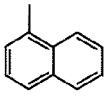
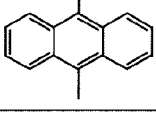
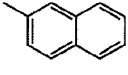
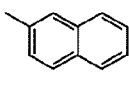
[0032]

(Table 5)

	X1	Ar1	Ar2
141			
142			
143			
144			
145			
146			
147			
148			
149			

[0033]

(Table 6)

	X1	Ar1	Ar2
150			
151			
152			
153			
154			

[0034]

An organic EL device provided by this invention comprises a secondary component, that is, a phosphorescent dopant material in its light-emitting layer. Any of the known phosphorescent metal complexes described in the aforementioned patent documents and non-patent documents can be used as a dopant material and these phosphorescent organic metal complexes preferably contain a metal selected from groups 7 to 11 of the periodic table at the center. This metal is preferably selected from ruthenium, rhodium, palladium, silver, rhenium, osmium, iridium, platinum, and gold. One kind or two kinds or more dopant materials or metals may be used.

Phosphorescent dopant materials are publicly known as described in the patent document 1 and elsewhere. Phosphorescent dopant materials are preferably phosphorescent ortho-metalated metal complexes or porphyrin metal complexes and

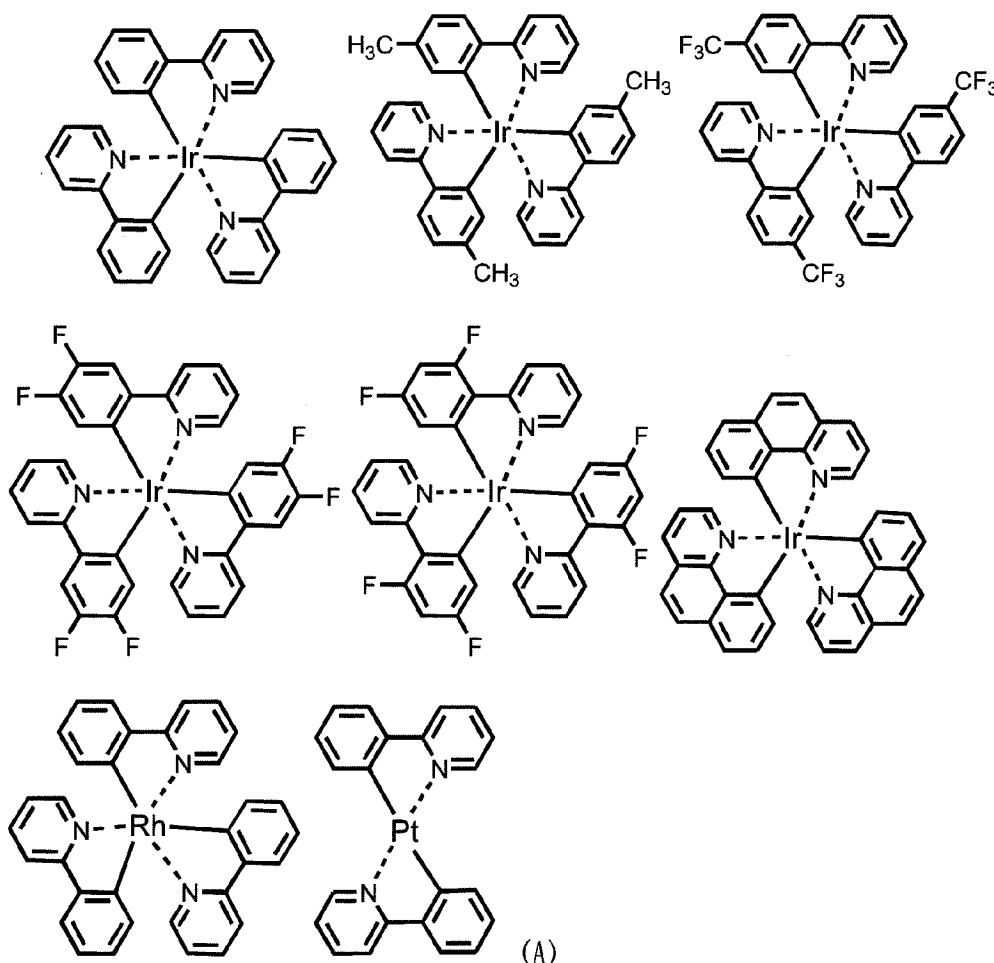
these metal complexes are publicly known as described in the patent document 5 and elsewhere. Therefore, these known phosphorescent dopant materials can be used freely.

[0035]

Examples of preferable organic metal complexes are complexes containing a noble metal element such as Ir at the center (formula A), typically Ir(Ppy)<sub>3</sub>, complexes such as Ir(bt)<sub>2</sub>·acac<sub>3</sub> (formula B), and complexes such as PtOEt<sub>3</sub> (formula C). Some of them are illustrated below, but the organic metal complexes useful for this invention are not limited to those illustrated below.

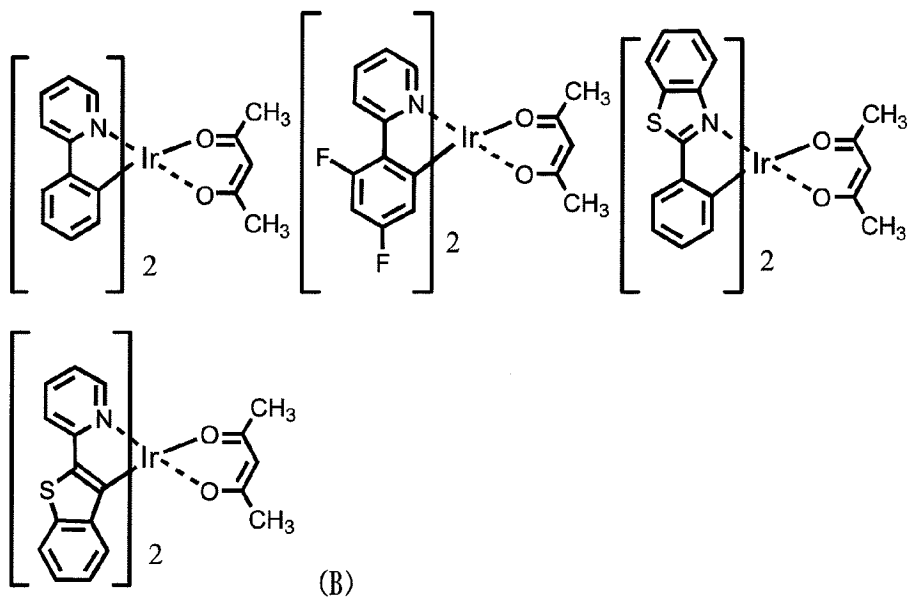
[0036]

(Chem 3)



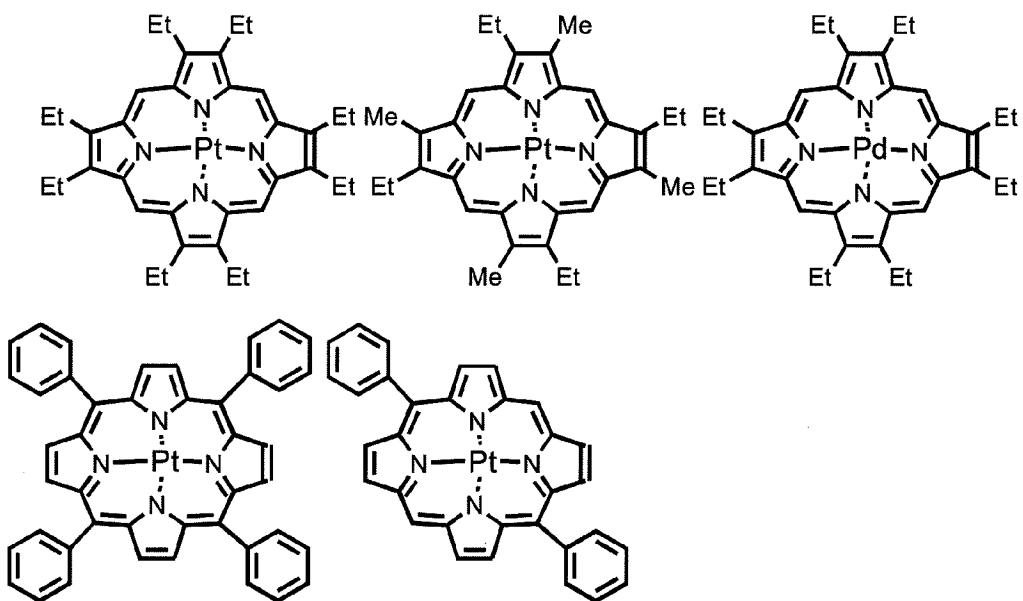
[0037]

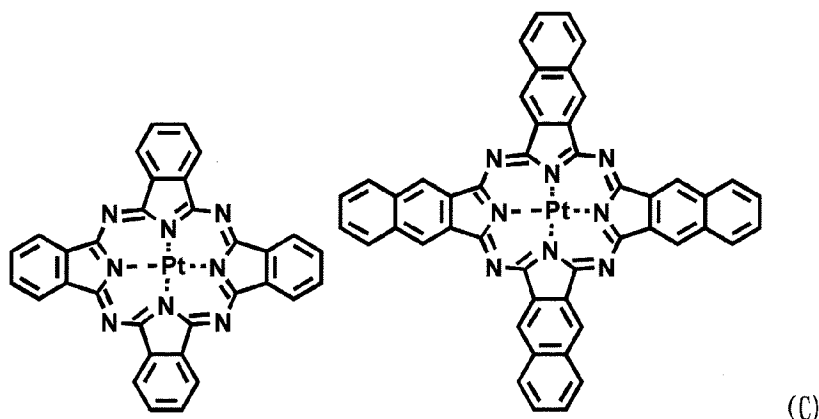
(Chem 4)



[0038]

(Chem 5)





### [Effect of the Invention]

[0039]

This invention provides a phosphorescent organic electroluminescent element with improved luminous efficiency, driving stability and heat resistance applicable to display devices such as flat panel displays and illuminating devices.

### [Preferred Embodiments of the Invention]

[0040]

An organic EL device provided by this invention will be explained with reference to the drawing. Fig. 1 is the cross section of a structure generally used for an organic EL device according to this invention; 1 denotes a substrate, 2 an anode, 3 a hole-injecting layer, 4 a hole-transporting layer, 5 a light-emitting layer, 6 a hole-blocking layer, 7 an electron-transporting layer, and 8 a cathode. Normally, 3 through 7 are organic layers and an organic EL device provided by this invention comprises one or more organic layers including the light emitting-layer 5. Advantageously, the device has three or more organic layers, preferably five or more organic layers, including the light-emitting layer 5. It is to be noted that the layered structure shown in Fig. 1 is merely an example and one or more layers may be added thereto or omitted therefrom.

[0041]

The substrate 1 supports an organic EL element and is made from a quartz or



glass plate, a metal plate or foil or a plastic film or sheet. In particular, transparent sheets of synthetic resins such as polyester, polymethacrylate, polycarbonate and polystyrene are desirable. When a synthetic resin is used for a substrate, it is necessary to take the gas barrier property of the resin into consideration. There is an undesirable possibility of the air passing through a substrate to degrade an organic EL element when the gas barrier property of the substrate is too poor. One of the remedial methods is to provide a dense silicon oxide film on at least one side of the synthetic resin substrate to secure the necessary gas barrier property.

[0042]

The anode 2 is provided on the substrate 1 and plays a role of injecting holes into the hole-transporting layer. The anode is usually constructed of a metal such as aluminum, gold, silver, nickel, palladium and platinum, a metal oxide such as oxide of indium and/or tin, a metal halide such as copper iodide, carbon black and conductive polymers such as poly(3-methylthiophene), polypyrrole and polyaniline. The anode 2 is usually formed by a technique such as sputtering and vacuum deposition. When fine particles of metal such as silver, copper iodide, carbon black, conductive metal oxides or conductive polymers are used, the particles are dispersed in a solution of a binder resin and applied to the substrate 1 to form the anode 2. Moreover, in the case of a conductive polymer, it is possible to form the anode 2 by forming a thin film of the polymer directly on the substrate 1 by electrolytic polymerization of the corresponding monomer or by coating the substrate 1 with the conductive polymer. The anode 2 may also be formed by piling different materials one upon another. The anode varies in thickness with the requirement for transparency. Where transparency is needed, it is preferable to keep the transmittance of visible light usually at 60% or more, preferably at 80% or more. In this case, the thickness is usually 5-1000 nm, preferably 10-500 nm. Where opaqueness is acceptable, the anode 2 may be the same as the substrate 1. It is possible to laminate a different conductive material on the aforementioned anode 2.

[0043]

A practice adopted for the purposes of enhancing the efficiency of hole injection and improving the adhesive strength of the organic layers as a whole to the anode is to interpose the hole-injecting layer 3 between the hole-transporting layer and the anode 2. The interposition of the hole-injecting layer 3 is effective for lowering the initial driving voltage of an element and at the same time suppressing a rise in voltage when an element is driven continuously at a constant current density.

The material selected for the hole-injecting layer must satisfy the following requirements: it produces a close contact with the anode; it is capable of forming a uniform thin film; it is thermally stable, that is, it has a melting point of 300 °C or above and a glass transition temperature of 100 °C. Still further, the material must have low ionization potential which facilitates hole injection from the anode and show high hole mobility.

[0044]

So far, phthalocyanine compounds such as copper phthalocyanine, organic compounds such as polyaniline and polythiophene, sputtered carbon membranes and metal oxides such as vanadium oxide, ruthenium oxide and molybdenum oxide have been reported as materials capable of attaining this object. In the case of an anode buffer layer, it is possible to form thin films in the same manner as for the hole-transporting layer. In the case of inorganic materials, it is further possible to use such methods as sputtering, electron beam evaporation and plasma CVD. The thickness of the hole-injecting layer 3 thus formed is usually 3-100 nm, preferably 5-50 nm.

[0045]

The hole-transporting layer 4 is provided on the hole-injecting layer 3. The material selected for the hole-transporting layer must be capable of injecting holes from the hole-injecting layer 3 at high efficiency and transporting the injected holes efficiently. To attain this object, the material must satisfy the following requirements:

it has low ionization potential, it is highly transparent against visible light, it shows high hole mobility, it is highly stable and it rarely generates impurities during manufacture or use that become traps. Still more, as the hole-transporting layer exists in contact with the light-emitting layer 5, it must not quench the light from the light-emitting layer nor form exciplexes between the light-emitting layer to lower the efficiency. Besides the aforementioned general requirements, heat resistance is additionally required where application to vehicular displays is considered. Hence, the material preferably has a Tg of 90°C or above.

[0046]

The compounds useful for such hole-transporting materials include aromatic diamines containing two tertiary amines whose nitrogen atoms are substituted with two or more aromatic condensed rings, aromatic amines of a starburst structure such as 4,4',4''-tris(1-naphthylphenylamino)triphenylamine, an aromatic amine consisting of a tetramer of triphenylamine and spiro compounds such as 2,2',7,7'-tetrakis-(diphenylamino)-9,9'-spirobifluorene. These compounds may be used singly or as a mixture.

[0047]

Besides the aforementioned compounds, the materials useful for the hole-transporting layer 4 include polymeric materials such as polyvinylcarbazole, polyvinyltriphenylamine and polyaryleneethersulfones containing tetraphenylbenzidine. When the coating process is used in forming the hole-transporting layer, a coating solution is prepared by mixing one kind or more of hole-transporting materials and, if necessary, binder resins that do not become traps of holes and additives such as improvers of coating properties, the solution is applied to the anode 2 or the hole-injecting layer 3 by a process such as spin coating and the solution is dried to form the hole-transporting layer 4. The binder resins here include polycarbonate, polyarylate and polyester. Addition of a binder resin in a large amount lowers the hole mobility and it is preferably kept at a low level, usually below

50 wt%.

[0048]

When the vacuum deposition process is used in forming the hole-transporting layer, the selected hole-transporting material is introduced to a crucible placed in a vacuum container, the container is evacuated to  $1 \times 10^{-4}$  Pa or so by a suitable vacuum pump, the crucible is heated to evaporate the hole-transporting material and the hole-transporting layer 4 is formed on the substrate 1 which is placed opposite the crucible and on which the anode has been formed. The thickness of the hole-transporting layer 4 is usually 5-300 nm, preferably 10-100 nm. The vacuum deposition process is generally used to form such a thin film uniformly.

[0049]

The light-emitting layer 5 is provided on the hole-transporting layer 4. The light-emitting layer 5 comprises the aforementioned host material and phosphorescent dopant material and, on application of an electrical field between the electrodes, the hole injected from the anode and migrating through the hole-transporting layer recombine with the electrons injected from the cathode and migrating through the electron-transporting layer 7 (or the hole-blocking layer 6) to excite the light-emitting layer thereby causing intense luminescence. The light-emitting layer 5 may contain other components, for example, non-essential host materials and fluorescent colorants to the extent that they do not damage the performance of this invention.

[0050]

A host material to be used in the light-emitting layer must show a high efficiency of hole injection from the hole-transporting layer 4 and also a high efficiency of electron injection from the electron-transporting layer 7 (or the hole-blocking layer 6). To achieve this end, the host material must satisfy the following requirements; its ionization potential has an adequate value, it shows high mobility of holes and electrons, it is electrochemically stable and it rarely generates impurities during manufacture or use that becomes traps. Still more, the material must not form

exciplexes between the neighboring hole-transporting layer 4 or the electron-transporting layer 7 (or the hole-blocking layer 6) to lower the efficiency. Besides the aforementioned general requirements, heat resistance is additionally required where application of an element to vehicular displays is considered. Therefore, the material preferably has a Tg of 80°C or above.

[0051]

In the cases where one of the organic metal complexes represented by the aforementioned formulas A-C is used as a dopant material, the content of the material in the light-emitting layer is preferably in the range of 0.1-30 wt%. A content of less than 0.1 wt% does not contribute to improvement of the luminous efficiency of an element while a content in excess of 30 wt% causes quenching of light by a change in the concentration due to dimerization of molecules of the organic metal complex and the like and, as a result, the luminous efficiency drops. In the conventional elements utilizing fluorescence (singlet), it is a desirable tendency for an organic metal complex to be in an amount somewhat larger than that of a fluorescent colorant (dopant) contained in the light-emitting layer. The organic metal complex may be contained partially or distributed nonuniformly in the direction of film thickness in the light-emitting layer. The thickness of the light-emitting layer 5 is usually 10-200 nm, preferably 20-100 nm.

[0052]

The light-emitting layer 5 is advantageously formed by the vacuum deposition process. A host material and a dopant material are introduced together to a crucible placed in a vacuum container, the container is evacuated to  $1 \times 10^{-4}$  Pa or so by a suitable vacuum pump, the crucible is heated to evaporate both host material and dopant material and both materials are deposited on the hole-transporting layer 4. The rates of deposition of the host material and dopant material are monitored separately to control the content of the dopant material in the host material.

[0053]

The hole-blocking layer 6 is formed on the light-emitting layer 5 so that the blocking layer contacts the light-emitting layer 5 on the cathode side and it is formed by a compound which is capable of playing a role of inhibiting the holes that are migrating through the hole-transporting layer from reaching the cathode and capable of transporting the electrons that are injected from the cathode in the direction of the light-emitting layer efficiently. The properties required for a material constituting the hole-blocking layer are high electron mobility and low hole mobility. The hole-blocking layer 6 has a function of confining holes and electrons in the light-emitting layer thereby improving the luminous efficiency.

[0054]

The electron-transporting layer 7 is formed from a compound which is capable of transporting the electrons that are injected from the cathode towards the hole-blocking layer 6 upon application of an electrical field between the electrodes. An electron-transporting compound useful for the electron-transporting layer 7 is required to show high efficiency of electron injection from the cathode 8 and have a high electron mobility to enable efficient transportation of the injected electrons.

[0055]

The materials satisfying these requirements include metal complexes such as 8-hydroxyquinoline aluminum complex (Alq<sub>3</sub>), 10-hydroxybenzo[h]quinoline metal complexes, distyrylbiphenyl derivatives, silole derivatives, 3- or 5-hydroxyflavone metal complexes, benzoxazole metal complexes, benzothiazole metal complexes, trisbenzimidazolylbenzene, quinoxaline compounds, phenanthroline derivatives, 2-*t*-butyl-9,10-N,N'-dicyanoanthraquinonedimine, n-type hydrogenated amorphous silicon carbide, n-type zinc sulfide and n-type zinc selenide. The thickness of the electron-transporting layer 7 is usually 5-200 nm, preferably 10-100 nm.

The electron-transporting layer 7 is formed on the hole-blocking layer 6 by a process such as coating or vacuum deposition as in the formation of the hole-transporting layer 4. The vacuum deposition process is normally used.

[0056]

The cathode 8 plays a role of injecting electrons to the light-emitting layer 5. A material useful for the cathode 8 may be the same as the aforementioned material for the anode 2. However, a preferred material is a metal of low work function such as tin, magnesium, indium, calcium, aluminum and silver and alloys thereof. Concrete examples are alloy electrodes of low work function such as magnesium-silver alloys, magnesium-indium alloys and aluminum-lithium alloys. Furthermore, insertion of an ultrathin insulating film (0.1-5 nm) of LiF, MgF<sub>2</sub>, Li<sub>2</sub>O and the like to the interface of the cathode and the electron-transporting layer is an effective method for improving the efficiency of an element. The thickness of the cathode 8 is usually the same as that for the anode 2. To protect a cathode made from a metal of low work function, the cathode is covered with a layer of a metal of high work function and good stability in the air and this improves the stability of an element. Metals such as aluminum, silver, copper, nickel, chromium, gold and platinum are used for this purpose.

[0057]

It is possible to obtain an element having a structure which is the reverse of the structure shown in Fig. 1: for example, one element is formed by piling one upon another the cathode 8, the hole-blocking layer 6, the light-emitting layer 5, the hole-transporting layer 4 and the anode 2 on the substrate 1 and another element is formed in such a manner as to have a structure of substrate 1/anode 8/electron-transporting layer 7/hole-blocking layer 6/light-emitting layer 5/hole-transporting layer 4/hole-injecting layer 3/anode 2.

[Examples]

[0058]

#### Synthetic Example 1

In a 300-ml four-necked flask equipped with a stirrer, a Dimroth condenser, and a thermometer were placed 10.9 g (0.27 mole) of sodium hydroxide, 52.7 g of ethanol,

and 98.3 g of deionized water. The mixture was stirred at room temperature for 10 minutes and, after confirmation of the dissolution of the sodium hydroxide, 26.1 g (0.22 mole) of acetophenone was added. Thereafter, the mixture was cooled by ice water and 14.1 g (0.11 mole) of terephthalaldehyde was added. After the addition, the mixture was heated under reflux with stirring for 4 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and a solid was collected by filtration. The solid was reslurried with ethanol and dried under reduced pressure to give 28.5 g of a yellow powder. This powder was analyzed by thin-layer chromatography to be a single product. Analysis of this product by mass spectrometry showed that its molecular weight was 338 and identical with that of the target product chalcone. The yield of the isolated product was 80.1%.

[0059]

#### Synthetic Example 2

In a 2000-ml four-necked flask equipped with a stirrer, a Dimroth condenser, and a thermometer were placed 20.1 g of potassium hydroxide and 1482.7 g of ethanol. The mixture was stirred at room temperature and, after confirmation of the dissolution of the potassium hydroxide (0.34 mole), 32.8 g (0.10 mole) of the chalcone obtained in Synthetic Example 1 was added at room temperature. Further, 40.4 g (0.37 mole) of phenylhydrazine was added at room temperature. After the addition, the mixture was heated under reflux with stirring for 2.5 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and a solid was collected by filtration. The solid was washed with methanol and hexane and dried under reduced pressure to give 42.1 g of a yellow powder. This powder was confirmed by thin layer chromatography to be a single product. Analysis of this product by mass spectrometry showed that its molecular weight was 518 and identical with that of the target pyrazoline compound. The yield of the isolated product was 83.7%.

[0060]

#### Synthetic Example 3

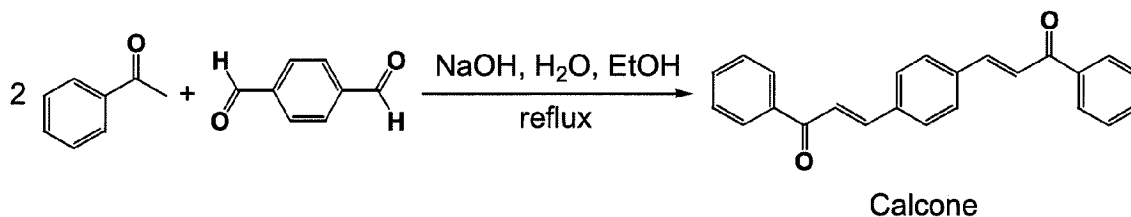


In a 500-ml four-necked flask equipped with a stirrer, a Dimroth condenser, and a thermometer was placed 354.4 g (4.256 moles) of pyridine. Then, 57.6 g (0.17 mole) of antimony pentachloride was added slowly in drops so that no vigorous generation of heat occurred. After the dropwise addition, the mixture was allowed to cool to room temperature and 25.9 g (0.050 mole) of the pyrazoline compound obtained in Synthetic Example 2 was added. After this addition, the mixture was stirred at room temperature for 3.5 hours. Upon completion of the reaction, a solid was recovered by filtration. The solid was washed with ethanol to give 42.1 g of a pale brown powder. The powder was recrystallized twice from methylene chloride to give 18.3 g of a product as white crystals. Analysis of the product by thin layer chromatography showed that the product consists of a single compound and analysis of the compound by mass spectrometry showed that its molecular weight was 514 and identical with that of the target compound 5,5'-(1,4-phenylene)bis[1,3-diphenyl-1H-pyrazole] (hereinafter referred to as PPB). The melting point was 246.8°C and the yield of the isolated product was 71.4%.

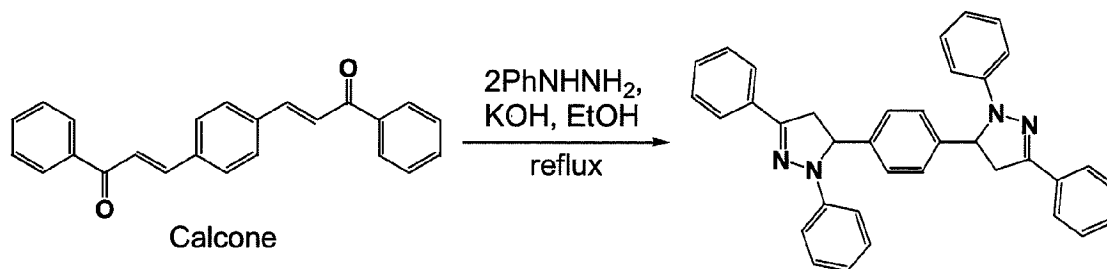
[0061]

The sequence of reactions in Synthetic Examples 1-3 are shown below.

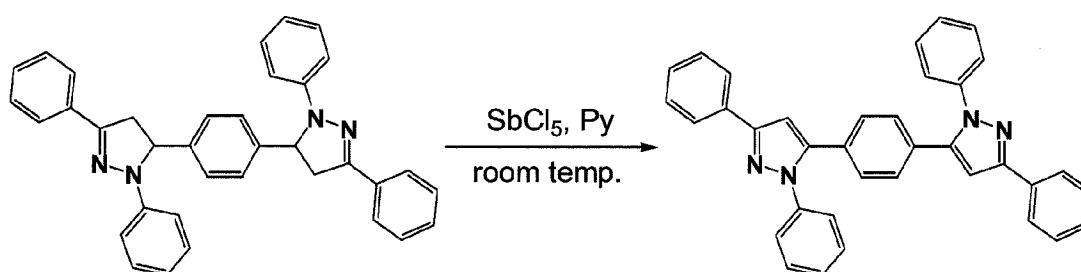
(Chem 6)



(Chem 7)



(Chem 8)



[0062]

The product obtained in Synthetic Example 3 or PPB was submitted to NMR analysis (performed by UNITY Plus-500SW manufactured by Varian) and to elemental analysis (performed by SUMIGRAPH NC-80 manufactured by Sumitomo Chemical Co., Ltd.) and the results are shown below.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.86 (s, 2H), 7.23 (s, 4H), 7.30 (m, 12H), 7.44 (dd, 4H,  $J = 0.15 \text{ Hz}, 6.0 \text{ Hz}$ ), 7.92 (d, 4H)

Elemental analysis (wt%): measured C 82.27, N 10.67; theoretical C 84.02, N 10.89

[0063]

To examine the heat-resistant characteristics of candidate compounds for the main component of the light-emitting layer (host material), the glass transition temperature ( $T_g$ ) of these compounds was measured by DSC. Of the compounds tested, PBP is the compound obtained in Synthetic Example 3 and TAZ, CBP, BCP, and OXD are already known as host materials. The results are shown in Table 7.

[0064]

(Table 7)

Host material	Glass transition temperature (T <sub>g</sub> ) (°C)
PBP	86
TAZ	— 1)
CBP	— 1)
BCP	— 1)
OXD	— 1)

1) Not observed on account of high crystallinity.

[0065]

## Example 1

An organic EL device having the layered structure shown in Fig. 1 less the hole-injecting layer 3 and the hole-blocking layer 6 was fabricated as follows.

The anode 2 was formed by patterning a 2 mm-wide stripe of a transparent conductive indium·tin oxide (ITO, manufactured by GEOMATEC Co., Ltd.) on the glass substrate 1, submitted successively to cleaning with pure water, ultrasonic cleaning with acetone, and ultrasonic cleaning with isopropyl alcohol, dried by nitrogen blowing, submitted finally to ultraviolet/ozone cleaning, and set up in an apparatus for vacuum deposition.

The aforementioned apparatus was exhausted preliminarily by an oil rotary pump and then exhausted by an oil diffusion pump equipped with a liquid nitrogen trap until the degree of vacuum in the apparatus reached  $3 \times 10^{-4}$  Pa to  $5 \times 10^{-4}$  Pa. The hole-transporting layer 4 was formed by heating a molybdenum boat containing N,N'-dinaphthyl-N,N'-diphenyl-3,3'-dimethyl-4,4'-diaminobiphenyl (HMTPD) and depositing the vapor to a film thickness of 60 nm. On this layer was formed the light-emitting layer 5 by co-depositing PBP as the primary component and tris(2-phenylpyridine)iridium complex (Ir(ppy)<sub>3</sub>) as a phosphorescent organic metal complex from different evaporation sources to a film thickness of 25 nm. The concentration of

Ir(ppy)<sub>3</sub> at this point was 7 wt%. Thereafter, a 50 nm-thick film of Alq<sub>3</sub> was formed as the electron-transporting layer 7.

The aforementioned device was taken out of the apparatus into the air, attached closely to a mask for vapor deposition of the cathode or a shadow mask in the form of a 2 mm-wide stripe so that the stripe met at right angles with the ITO stripe of the anode 2 and set up in another vacuum apparatus. The apparatus was exhausted in the same manner as in the deposition of the organic layers and lithium fluoride (LiF) was deposited to a film thickness of 0.5 nm as the electron-injecting layer and aluminum was deposited to a film thickness of 170 nm as the cathode on the electron-transporting layer.

[0066]

The organic electroluminescent device thus obtained was connected to an external power source and, upon application of direct current voltage, was confirmed to show the light-emitting characteristics shown in Table 8. In Table 8, the luminous efficiency is a value measured at 1000 cd/m<sup>2</sup>, the luminance/current means the slope of luminance-current density characteristics, and the voltage is a value measured at 1000 cd/m<sup>2</sup>. The luminance/voltage characteristics are shown in Fig. 2. The maximum wavelength of the spectrum observed in emission of light from the device is 515 nm and this confirms that Ir(ppy)<sub>3</sub> emits light.

[0067]

#### Comparative Example 1

An organic electroluminescent device was fabricated as in Example 1 with the exception of using 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) as the primary component of the light-emitting layer. The characteristics of this device are shown in Table 8 and Fig. 2.

[0068]

(Table 8)

	luminance/current ( cd/A )	voltage ( V ) @1000cd/m2	luminous efficiency ( lm/W ) @1000cd/m2
Example 1	41.03	12.2	10.30
Comparative Example 1	26.11	13.4	7.13

[Brief Description of the Drawing]

[0069]

Fig. 1 is a schematic cross section showing the layered structure of an organic EL device.

Fig. 2 is a graph showing the luminance-voltage characteristics.

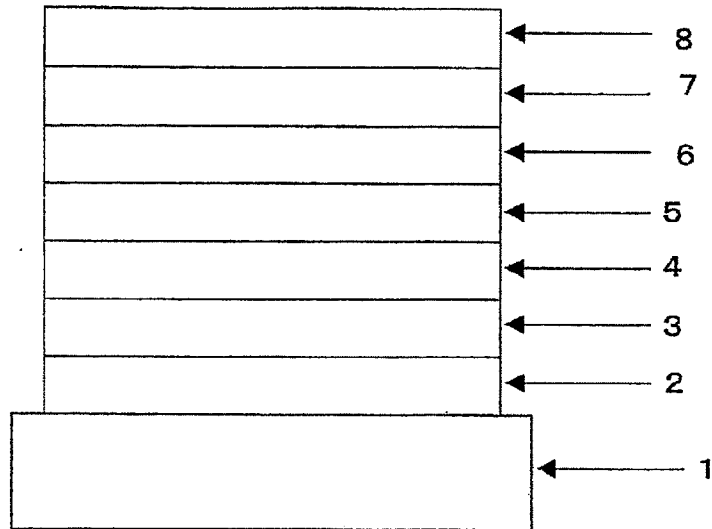
[Numbering in the Drawing]

[0070]

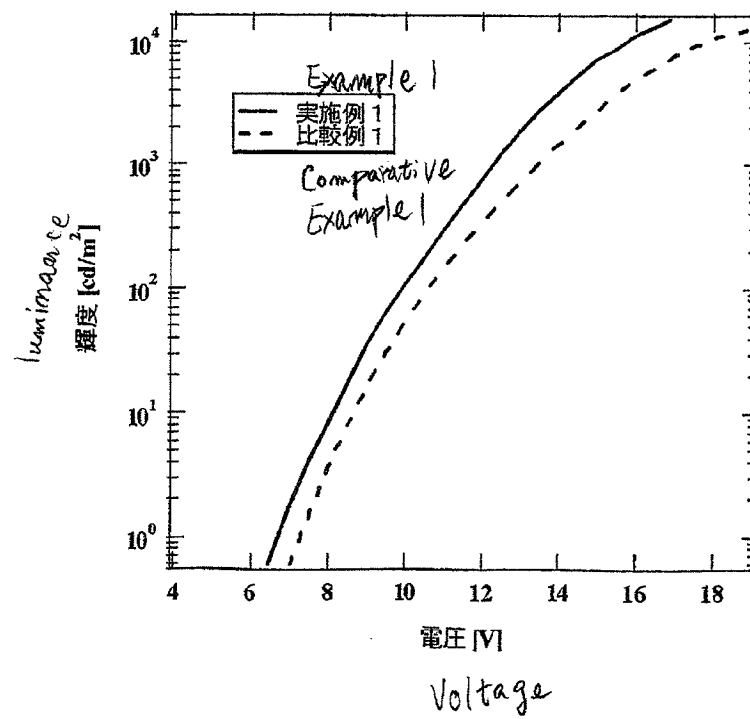
- 1, substrate;
- 2, anode;
- 3, hole-injecting layer;
- 4, hole-transporting layer;
- 5, light-emitting layer;
- 6, hole-blocking layer;
- 7, electron-transporting layer;
- 8, cathode.

[Name of Document] Drawing

[Fig. 1]



[Fig. 2]



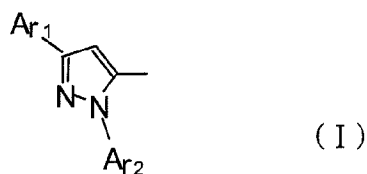
[Name of Document] Abstract

[Abstract]

[Problems] This invention provides an organic electroluminescent element (organic EL element) utilizing phosphorescence which emits light efficiently with high luminance at low current density, shows good driving stability and is applicable to display devices such as flat panel displays and illuminating devices.

[Means to Solve] The element comprises an anode, organic layers and a cathode piled one upon another on a substrate, at least one of the organic layers is a light-emitting layer containing a host material and a dopant material and a pyrazole-derived compound having 2-4 pyrazole structures represented by the following formula I in the same molecule is used as said host material;

[Chem 1]



wherein, Ar<sub>1</sub>-Ar<sub>2</sub> are independently hydrogen or substituted or unsubstituted aromatic hydrocarbon groups and at least one of Ar<sub>1</sub>-Ar<sub>3</sub> is a group other than hydrogen.

[Selected Figure] Fig. 1